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Reactions of fluoroalkanesulfonyl azides with cyclic vinyl ethers

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Abstract

The addition reactions of fluoroalkanesulfonyl azides to dihydropyran or dihydrofuran were studied. These reactions do not give the corresponding *N*-fluoroalkanesulfonyl azilidines but *N*-fluoroalkanesulfonyl-tetrahydropyranon-2-imines or *N*-fluoroalkanesulfonyl-tetrahydro-furano-2-imines. The reaction mechanism is discussed.

Keywords: Fluoroalkanesulfonyl azide; Cyclic vinyl ether; 1,3-Dipolar cycloaddition; *N*-Fluoroalkanesulfonyl-tetrahydropyranon-2-imine

1. Introduction

The reaction of organic azides with vinyl ethers was first studied by Franz and Osuch in 1963 [1,2]. Since then many research works in this area have been reported. For example, Huisgen et al. [3] reported that arylazides reacted with vinyl ethers to give corresponding stable cyclic triazolines, while Rectorr and Harmon [4] obtained *N*-arylsulfonyl-δ-pentane imidolactones from the reaction of arylsulfonyl azides with dihydropyran. Recently, Semenov [5,6] reported that the bicyclic 1-tosyl-5-ethoxy-1,2,3-triazoline formed in the reaction of tosyl azides with 1-ethoxy cyclopentene was transformed into the unstable bicyclic 1-tosyl-2-ethoxyazidine which then isomerized to *N*-(2-ethoxy-1-cyclopentenyl)-tosylamide (Scheme 1).

The reactions of perfluoroalkanesulfonyl azide, which was first synthesized from the reaction of trifluoromethanesulfonic acid anhydride with sodium azide in 1965 [7], has not been studied as extensively as its hydrocarbon analogues. One paper reported the reaction of $CF_3SO_2N_3$ with benzene as a trifluoromethanesulfonyl nitrene precursor [8]. Recently, we have investigated the photolysis and thermolysis of per- or polyfluoroalkanesulfonyl azides and found the per- or polyfluoroalkanesulfonyl nitrene formed reacted readily with alkenes, cyclohexene, dimethyl sulfide, triphenylphosphine, nitrosobenzene, etc. to afford the insertion or addition products [9,10]. As an extension of the exploration of fluoroalkanesulfonyl azides, we studied thermal reactions of $R_fSO_2N_3$ with cyclic vinyl ethers. Herein we wish to report these results.

In our previous work on the $R_fSO_2N_3$ **1** [9] we have found that no reaction occurred when **1** was refluxed with cyclohexene or 2,3-dimethylbutene for 8 h. Under irradiation, however, the nitrogen was released and the cycloproducts *N*-fluoroalkanesulfonyl azilidines were obtained. In these reactions, the fluoroalkanesulfonyl nitrene intermediates were involved.

Recently we [11] also reported the reaction of **1** with enamines, this reaction proceeded smoothly at 0 °C, the nitrogen gas was liberated spontaneously and gave the corresponding *N*-fluoroalkanesulfonyl imines (Scheme 2). Because the thermal decomposition temperature of **1** is 110 °C, it is clear that in this reaction the nitrene intermediate is not involved.

2. Results and discussion

Similar to enamines [11], vinyl ethers which contain an electron-rich double bond reacted readily with **1**. At room temperature, addition of **1** to an excess of dihydropyran **3** or to a stoichiometric amount of dihydropyran in a solvent (such as CH_2Cl_2 or C_6H_6), resulted in nitrogen gas evolution within 30–120 min, depending on the solvent, and fluoroalkyl groups. The products **5** were separated and purified by fractional vacuum distillation from the reaction mixture. Under same reaction condition, treatment of the azides **1** with dihydrofuran **2** gave reaction products **4**, which were similar to the products **5**.

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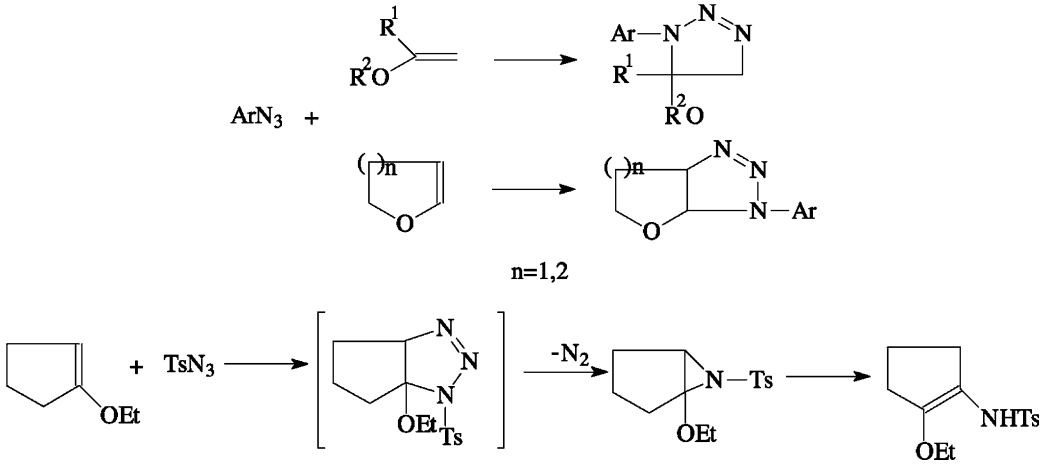
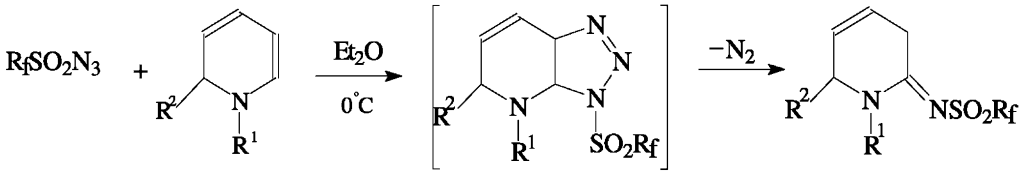


Scheme 1.

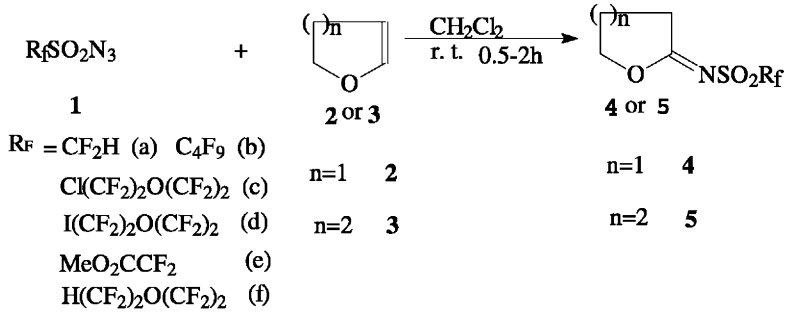


Scheme 2.

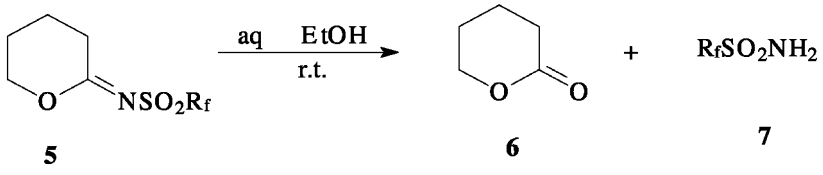
According to the IR and NMR spectra, the products were not the expected *N*-fluoroalkanesulfonyl azilidine [12], but *N*-fluoroalkanesulfonyl-tetrahydrofurano (or pyrano)-2-imines **4** and **5**. The IR spectra of the compounds **4** and **5** are quite similar. They have a strong absorption band in the range of 1590–1610 cm^{-1} for the –C=NSO_2 function [13], and did not exhibit a peak at 1190 cm^{-1} which is the characteristic absorption of ring-fused aziridines [14].

The ^{1}H NMR spectra of **5** shows four cyclic methene groups at 1.56–1.96 ppm (2 × CH_2), 2.60–2.86 ppm (1 × CH_2) and 4.05–4.56 ppm (OCH_2), respectively. In the ^{13}C NMR spectra of **5**, the signal at 176 ppm was consistent with the carbon atom of the C=N double bond (Scheme 3).

The structure of **5** was also confirmed by its hydrolysis. It readily hydrolyzed to give fluoroalkanesulfonylamide and δ-valerolactone (Scheme 4). We also found that the compound **5** was partly transformed to **6** and **7**, when it was stored at



Scheme 3.



Scheme 4.

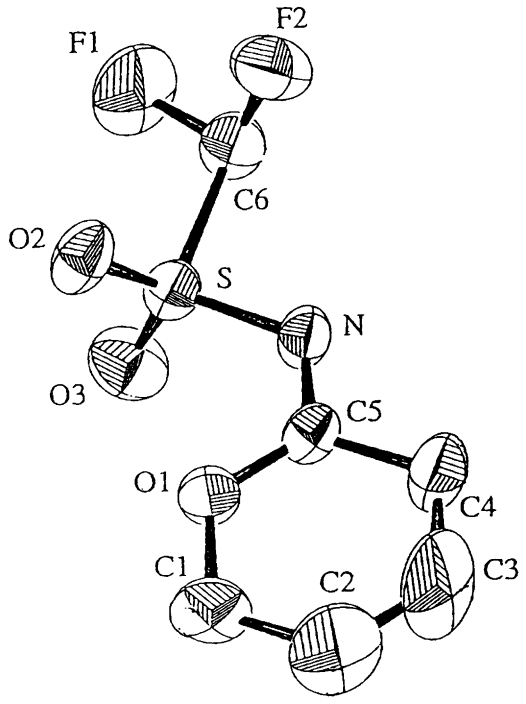


Fig. 1. The molecular structure of **5a**.

Table 1
Selected bond lengths (Å) and angles (°) of compound **5a**

Bond lengths (Å)		Base angles (°)	
O(1)–C(5)	1.317(5)	N–C(5)–O(1)	119.9(4)
C(5)–N	1.286(5)	O(1)–C(5)–C(4)	121.1(4)
N–S	1.614(4)	C(4)–C(5)–N	119.0(4)
S–O(3)	1.428(3)	C(5)–O(1)–C(1)	122.5(4)
S–(C6)	1.816(5)	S–N–C(5)	121.6(3)
O(1)–C(1)	1.462(5)	O(2)–S–O(3)	118.4(2)

room temperature for 1 week, about 40% decomposed according to the ^{19}F NMR spectra.

Similar behavior was also found in the case of R_fSO_2-N=CHOR prepared from the reaction of R_fSO_2N=S=O with HCO_2R, which was very easy to hydrolyze to the corresponding R_fSO_2NH and HCO_2R [15].

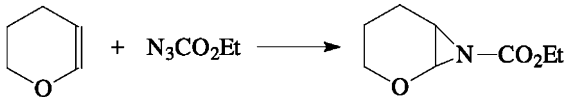
The structure of **5** was further confirmed by X-ray diffraction analysis, which was accomplished in a sealed capillary. The molecular structure of **5a** is shown in Fig. 1.

The bond lengths of C_5–N (1.29 Å), C_5–O (1.32 Å), N–S (1.61 Å), and the bond angles: N–C_5–O (119°), N–C_5–C_4 (119°), O_1–C_5–C_4 (121°) indicated the electron delocalisation in this molecule, and the four atoms (O, C_5, N, S) are planar (see Table 1). This structure is very similar to the structure of *N*-perfluoroalkanesulfonylformamide R_fSO_2=NCHNR_2 in which the bond lengths of N–C, N–C, and N–S are 1.29, 1.33, and 1.57 Å, respectively. However, R_fSO_2N=CHOR is very stable and does not hydrolyze even under acidic or basic reaction conditions [14].

When the reaction was carried out in benzene same products were obtained, but in a little longer reaction time (2–2.5 h) (see Table 2).

Table 2
Reaction result of azides **1** with cyclic vinyl ethers **2** or **3**

Entry	Azide **1**	Vinyl ethers **2** or **3**	Solvent	Time (h)	Products **4** or **5**	Yield (%)
1	**1c**	**2**	CH_2Cl_2	0.5	**4c**	70
2	**1c**	**2**	C_6H_6	2.5	**4c**	68
3	**1f**	**2**	CH_2Cl_2	0.5	**4f**	72
4	**1a**	**3**	CH_2Cl_2	0.5	**5a**	70
5	**1a**	**3**	C_6H_6	2.0	**5a**	68
6	**1b**	**3**	CH_2Cl_2	0.5	**5b**	65
7	**1c**	**3**	CH_2Cl_2	0.5	**5c**	60
8	**1d**	**3**	CH_2Cl_2	2.5	**5d**	62
9	**1e**	**3**	CH_2Cl_2	0.5	**5e**	68

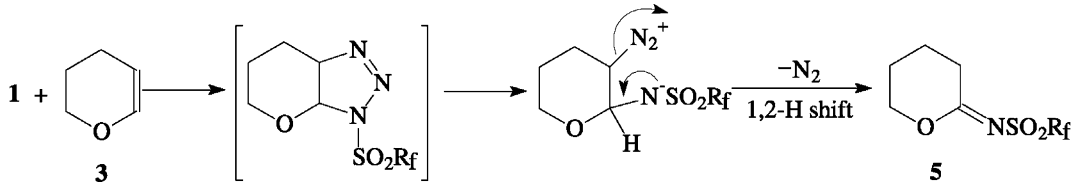


Scheme 5.

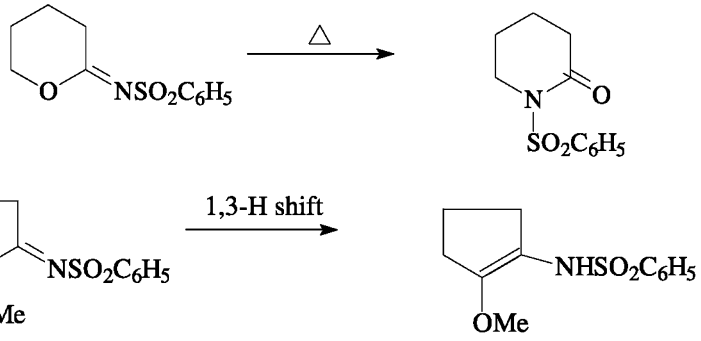
Brown and Edwards [16] reported that the reaction of ethylazidoformate and dihydropyran yielded an aziridine intermediate (see Scheme 5).

In contrast to ethyl azidoformate the reactions of fluoroalkanesulfonyl azides with dihydropyran do not proceed via fluoroalkanesulfonyl nitrenes. We postulate that the unstable triazoline should be firstly formed by 1,3-dipolar cycloaddition of **1**–**3**, which decomposed releasing the nitrogen gas followed by 1,2-H shift to give the product **5** (see Scheme 6). This sequence also resembles the mechanism proposed for the reaction of **1** with enamines [9].

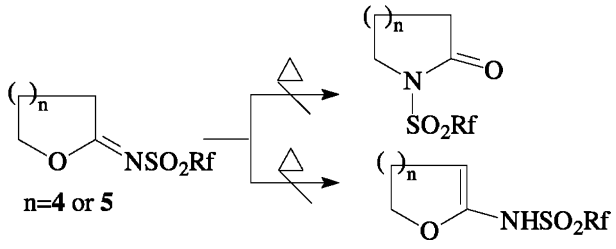
Literature [2] has reported that *N*-phenylsulfonyl-tetrahydropyranon-2-imine rearranged to *N*-phenylsulfonyl-2-piperidone on heating, while *N*-arylsulfonylimines of



Scheme 6.



Scheme 7.



Scheme 8.

5-methoxy-cyclo-pentanone converted into *N*-(2-methoxy-1-cyclopentenyl) sulfonylamides by 1,3-H shift [5,6] (Scheme 7).

Compounds **4** and **5** did not undergo such rearrangements and are stable on heating (Scheme 8).

3. Conclusion

In this paper, we report the reaction of fluoroalkanesulfonyl azides with cyclic vinyl ethers which did not lead to *N*-fluoroalkanesulfonyl aziridines. In this reaction, dihydropyran or dihydrofuran acted as the dipolarophile and reacted with azides to give unstable triazoline intermediates which then decomposed to zwitterionic structures with the loss of N_2 followed by the 1,2-H shift to produce the single product, fluoroalkanesulfonylimine. This proceeded more rapidly in polar solvent, but the nature of the solvent did not influence the reaction product and yield.

4. Experimental

^{1}H NMR and ^{19}F NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-300 spectrometer operating at 282 MHz for ^{19}F (internal standard $CFCl_3$) and 300 MHz for ^{1}H (internal standard TMS). Highfield shifts from TMS and CCl_3F are negative. IR spectra were obtained with a Perkin-Elmer 983G spectrophotometer using KBr disks. Lower resolution mass spectra and high resolution mass spectra (HRMS) were obtained on a Finnigan GC–MS 4021 and Finnigan MAT-8430 instrument, respectively.

4.1. General procedure of the reaction of fluoroalkaneazides with 3,4-dihydro-2H-pyran or dihydrofuran

A solution of **1a** (1.57 g, 10 mmol) in CH_2Cl_2 (5 ml) was added over a 10 min period to a solution of **3** (0.9 g, 10.7 mmol) in CH_2Cl_2 (5 ml). This reaction mixture was stirred at 20 °C for 1 h, after which the TLC analysis showed completeness of the reaction. The solvent and an excess of **3** was distilled off. Vacuum distillation gave crude product **5a** (1.5 g, 70.4%) containing small amount of $HCF_2SO_2NH_2$. Redistillation gave pure **5a**.

*4.1.1. N-Difluoromethylsulfonyl-tetrahydropyrano-2-imine (**5a**)*

FT-IR (ν_{max}, cm^{-1}): 2890, 2890 (s, C–H), 1600 (s, C=N), 1330 (vs, SO_2), 1120 (s, C–O), 1050 (s, C–F); ^{1}H NMR δ (ppm): 1.96 (m, 4H, 2 × CH_2), 2.73 (t, 2H, CH_2), 4.55 (t, 2H, CH_2O), 6.25 (t, 1H, HCF_2); ^{19}F NMR δ (ppm): 125.3 (d^2, J_{HF} = 52 Hz, CF_2); MS *m/z* (ion, %): 214 (M^+H, 100), 162 (M^+–HCF_2, 99), 130 ($C_5H_8ONS^+$, 17), 85 (M^+H–HF_2SO_2N, 79), 51 (HCF_2^+, 20); Anal. Calcd. for $C_6H_9F_2NO_3S$: C 33.80%, H 4.22%, N 6.57%. Found: C 33.53%, H 4.19%, N 6.47%.

*4.1.1.1. Crystal structure data of the compound **5a**.* $C_6H_9F_2NO_3S$: M = 213.18, monoclinic, space group $P2/c$, a = 8.869(3) Å, b = 5.862(2) Å, c = 171523(9) Å, β = 98.66(4) Å, v = 900.6(6) Å^3, Z = 4, Dc = 1.557 g/cm^3. Absorption coefficient = 3.66 cm^{-1}, $F(000)$ = 432.00. Radiation, Mo Kα (λ = 0.71069 Å). Crystal dimensions: 0.20 mm × 0.20 mm × 0.40 mm. Intensity data were collected at 293 K with a Rigaku AFC7R diffractometer using graphite-monochromated. Mo Kα radiation (μ = 3.6 cm^{-1}). A total of 1475 independent reflections were measured in the range 23.8 < 2θ < 25.6°. The structure was solved by direct methods and expanded using Fourier techniques. The positions for all H atoms were obtained by theoretical calculations. All positional parameters and anisotropic thermal parameters for non-H atom were refined by means of a full-matrix-least-squares technique. The final R and Rw values were 0.049 and 0.0705, respectively, based on 955

observed reflections ($I > 3.00(I)$). All calculations were performed on a Micro VAXII computer with SHELX86 and ORTEP programs. (All X-ray data have been deposited in Cambridge No. CCDC 188182.)

4.1.2. N-Perfluorobutylsulfonyl-tetrahydropyrano-2-imine (**5b**)

FT-IR (ν_{max}, cm^{-1}): 2963, 2910 (s, C–H), 1630 (s, C=N), 1330 (vs, SO_2), 1110 (s, C–F), 1030 (s, C–O); ^1H NMR δ (ppm): 1.88–1.98 (m, 4H, 2 × CH_2), 2.68–2.72 (m, 2H, CH_2), 4.52–4.55 (m, 2H, OCH_2); ^{19}F NMR δ (ppm): 81.7 (s, CF_3), −114.8 (s, CF_2), −121.6 (s, CF_2), −126.5 (s, CF_2); MS *m/z* (ion, %): 382 (M^+ + 1, 50), 381 (M^+, 22), 219 (C_4F_9, 11), 162 (M^+–C_4F_9, 49), 98 (M^+–$SO_2C_4F_9$, 11), 84 (M^+–$NSO_2C_4F_9$, 9); Anal. Calcd. for $C_9H_8F_9NO_3S$: C 28.35%, H 2.01%, N 3.67%. Found: C 28.05%, H 2.05%, N 3.72%.

4.1.3. (5′-Chloro-3′-oxa-octafluoropentyl)-sulfonyl-tetrahydropyrano-2-imine (**5c**)

FT-IR (ν_{max}, cm^{-1}): 2980, 2910, 2820 (s, C–H), 1595 (s, C=N), 1345 (vs, SO_2), 1150 (s, C–O); ^1H NMR δ (ppm): 1.65–2.00 (m, 4H, 2 × CH_2), 2.80 (m, 2H, CH_2), 3.87 (m, 2H, OCH_2); ^{19}F NMR δ (ppm): −74.3 (s, $ClCF_2$), −80.1 (m, 2F, OCF_2), −87.0 (m, 2F, OCF_2), −118.3 (s, 2F, SCF_2); MS *m/z* (ion, %): 413(M^+, 12), 379 (M^+H–Cl, 9), 360 (M^+H–Cl–F, 3), 135 ($ClCF_2CF_2^+$, 38), 98 ($C_5H_8ON^+$, 11), 85 ($C_5H_9O^+$, 80), 84 ($C_5H_8O^+$, 24), 64 (SO_2^+, 100); Anal. Calcd. for $C_9H_8ClF_8NO_4S$: C 26.12%, H 1.93%, N 3.38%. Found: C 26.35%, H 2.06%, N 3.16%.

4.1.4. (5′-Iodo-3′-oxa-octafluoropentyl)-sulfonyl-tetrahydropyrano-2-imine (**5d**)

FT-IR (ν_{max}, cm^{-1}): 2990, 2910 (s, CH), 1595 (s, C=N), 1345 (s, SO_2), 1145, 1050 (s, C=O); ^1H NMR δ (ppm): 1.66 (m, 4H, 2 × CH_2), 2.88 (m, 2H, CH_2), 4.10 (m, 2H, OCH_2); ^{19}F NMR δ (ppm): −69.0 (s, ICF_2), −81.8 (m, OCF_2), −86.1 (m, OCF_2), −119.1 (s, SCF_2); MS *m/z* (ion, %): 505 (M^+, 6), 379 (M^+H–I, 5), 360 (M^+H–I–F, 3), 227 ($ICF_2CF_2^+$, 18), 98 ($C_5H_8ON^+$, 10), 85 ($C_5H_9O^+$, 80), 84 ($C_5H_8O^+$, 24), 64 (SO_2^+, 100); Anal. Calcd. for $C_9H_8F_8INO_4S$: C 31.39%, H 1.58%, N 2.77%. Found: C 31.21%, H 1.62%, N 3.08%.

4.1.5. (2′-Methoxylcabonyl-1′-difluoromethyl)-sulfonyl-tetrahydropyrano-2-imine (**5e**)

FT-IR (ν_{max}, cm^{-1}): 2950 (s, C–H), 1780 (vs, C=O), 1601 (s, C=N), 1340 (s, SO_2), 1160 (s, C–O); ^1H NMR δ (ppm): 1.86 (m, 4H, 2 × CH_2), 2.63 (m, 2H, CH_2), 3.83 (s, OCH_3), 4.63 (t, 2H, OCH_2); ^{19}F NMR δ (ppm): −109.5 (s, 2F, CF_2); ^{13}C NMR δ (ppm): 16.94 (CH_3), 21.20 (CH_2), 28.68 (CH_2), 54.36 (CH_2),73.39 (OCH_2), 112.12 (t^2, J_{CF} = 290 Hz, CF_2), 159.78 (t^3, J_{CF} = 28.7 Hz, C=O), 176.54 (C=N); MS *m/z* (ion, %): 272 (M^+H, 54), 253 (M^+–F, 22), 208 (M^+–SO_2, 2), 204 (M^+–C_5H_8, 13), 190 (M^+H–C_5H_8–N, 28), 119 ($MeO_2CCF_2^+$, 16), 101 (MeO_2CNCO^+, 16), 98 ($C_5H_8ON^+$, 54), 84 ($C_5H_8O^+$, 18), 59 (MeO_2C^+, 24); Anal. Calcd. for $C_8H_{11}F_2NO_5S$: C 35.42%, H 4.06%, N 5.17%. Found: C 35.79%, H 4.37%, N 4.98%.

4.1.6. (5′-Chloro-3′-oxa-octafluoropentyl)-sulfonyl-tetrahydrofurano-2-imine (**4c**)

FT-IR (ν_{max}, cm^{-1}): 2972 (s, C–H), 1630 (s, C=N), 1356, 1309 (s, SO_2) 1180, 1144 (s, C–O); ^1H NMR δ (ppm): 2.29–2.34 (m, 2H, CH_2), 3.03 (m, 2H, CH_2–C=N), 4.61–4.65 (m, 2H, OCH_2); ^{19}F NMR δ (ppm): −74.3 (s, $ClCF_2$), −82.0 (m, 2F, OCF_2), −87.1 (m, 2F, OCF_2), −114.8 (s, 2F, SCF_2); MS *m/z* (ion, %): 400/402 (M^+ + H, 100/37), 364 (M^+–Cl, 4), 147 (M^+H–R_f, 65), 84 (M^+H–SO_2R_f, 13); Anal. Calcd. for $C_8H_{6Cl}F_8NO_4S$: C 24.03%, H 1.50%, N 3.50%. Found: C 23.88%, H 1.38%, N 3.69%.

4.1.7. (1′,1′,2′,2′,4′,4′,5′,5′-Octafluoro-3′-oxa-pentyl)-sulfonyl-tetrahydrofurano-2-imine (**4f**)

FT-IR (ν_{max}, cm^{-1}): 2966 (CH), 1627 (C=N), 1360, 1330 (s, SO_2), 1258, 1179, 1143 (s, C–O); ^1H NMR δ (ppm): 2.33–2.43 (m, 2H, CH_2), 3.08–3.13 (m, 2H, CH_2–C=N), 4.68–4.73 (m, 2H, OCH_2), 5.88 (m, 1H, CF_2H); ^{19}F NMR δ (ppm): −81.4 (m, 2F, OCF_2), −89.1 (m, 2F, OCF_2), −118.0 (s, 2F, SCF_2), −138.2 (t, 2F, HCF_2); MS *m/z* (ion, %): 366 (M^+ + H, 41), 148 (M^+–R_f, 100), 101 ($CF_2CF_2H^+$, 25); Anal. Calcd. for $C_8H_7F_8NO_3S$: C 26.31%, H 1.93%, N 3.84%. Found: C 26.41%, H 1.98%, N 3.81%.

Acknowledgements

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